

On the Nernst equation in electrochemistry

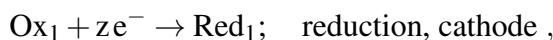
Theoretical background: Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods*, Ch. 2.
(Novák Mihály, Szűcs Árpád, *Elektrokémia*, Ch. 9 (Hungarian)).

Type of practice: Individual.

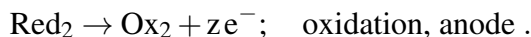
Purpose of practice: Experimental study of the basic equation of equilibrium electrochemistry, the Nernst equation, with a simple redox system.

1 Introduction

An electrochemical cell contains at least two electron-conducting – ion-conducting phase boundaries, so-called half-cells (electrodes in the broader sense). In one of them, under suitable conditions, reduction can occur:

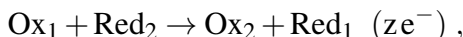


where e^- represents the electron, and z is the charge transfer number. In the other half-cell, under suitable conditions, oxidation can occur:



Red_1 , Red_2 , Ox_1 and Ox_2 can be in solid, liquid and gas phase, or in the form of an electrolyte solution. If Red is a metal and Ox is the ion of this metal in a solution phase, then we talk about a metal electrode (e.g., $\text{Zn}|\text{Zn}^{2+}(\text{aq})$ system). If one of Ox or Red is in the gas phase, then we talk about a gas electrode (e.g., $\text{H}_2|\text{H}^+(\text{aq})$ system). Then the electron conducting phase is a so-called inert, indifferent electrode. Inert, because it is chemically resistant in the given medium, indifferent, because it is not involved chemically in the process, *only* as an electron source or as an electron sink. If Ox and Red are in the same phase, then we talk about a redox electrode (e.g., $\text{Fe}^{3+} + \text{Fe}^{2+}$ system). Then the electron-conducting phase is also an inert, indifferent electrode. Such a system will be studied in the practice.

The cell reaction is the sum of the two half-cell reactions (electrode reactions):



where $(z\text{e}^-)$ indicates that the process would mean the transfer of z mol electrons (thus $-z \cdot F$ charge) from the anode to the cathode. $F = e \cdot N_A$ is the Faraday constant (the molar elemental charge), where e is the elementary charge and N_A is the Avogadro constant.

The change in Gibbs energy (earlier it was called free enthalpy, Gibbs free energy) during the reaction (ΔG_r), shortly reaction Gibbs energy (i.e., energy change in isothermal, isobaric, reversible conditions without a change in composition so that the amount of substances corresponding to the stoichiometric numbers in the equation reacts), i.e., the maximal useful (nonmechanical pressure–volume) work ($w_{\max}$) can be given as the derivative of the Gibbs energy with respect to the reaction coordinate (ξ). By definition, the reaction coordinate is

$$d\xi = \frac{dn_i}{\nu_i},$$

where dn_i is the change in the amount of substance of the i -th component and ν_i is the stoichiometric coefficient of this component in the reaction equation. Based on these,

$$\Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_{i=1}^n \nu_i \cdot \mu_i,$$

where μ_i is the chemical potential of the component, i.e., its partial molar Gibbs energy,

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{p,T,n_{j \neq i}}.$$

The chemical potential depends on the composition,

$$\mu_i = \mu_i^0 + RT \ln a_i,$$

where μ_i^0 is the standard chemical potential of the i-th component and a_i is the activity. Summarizing the above,

$$\Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_{i=1}^n \nu_i \cdot \mu_i = \sum_{i=1}^n \nu_i \cdot \mu_i^0 + RT \ln \prod_{i=1}^n a_i^{\nu_i}.$$

The reaction Gibbs energy, can also be electrical work. That is, to the transfer of z mol of electron ($-z \cdot F$ charge) from the anode to the cathode we can assign a potential difference (cell voltage) by which we do the same work. Electrical work can be given as the product of voltage (U) and passed charge (Q_{electron}), i.e.,

$$w = U \cdot Q_{\text{electron}}, \quad \text{so}$$

$$\Delta G_r = w_{\text{max}} = -z \cdot F \cdot E_{\text{cell}},$$

where E_{cell} is the maximal potential difference that can develop in the cell. This is the so-called cell reaction potential (in American literature it is often denoted as E_{rxn}). Thus,

$$\Delta G_r = \sum_{i=1}^n \nu_i \cdot \mu_i^0 + RT \ln \prod_{i=1}^n a_i^{\nu_i} = -z \cdot F \cdot E_{\text{cell}}, \quad \text{i.e.,}$$

$$E_{\text{cell}} = \frac{\Delta G_r}{-zF} = \frac{\sum_{i=1}^n \nu_i \cdot \mu_i^0}{-zF} + \frac{RT}{-zF} \ln \prod_{i=1}^n a_i^{\nu_i}, \quad \text{which -after rearranging- results in}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{zF} \ln \prod_{i=1}^n a_i^{\nu_i} = E_{\text{cell}}^0 - \frac{RT}{zF} \ln Q,$$

where E_{cell}^0 is the standard cell reaction potential and Q is the reaction quotient. *This is the so-called Nernst equation.* It is obvious, that

$$E_{\text{cell}}^0 = \frac{\sum_{i=1}^n \nu_i \cdot \mu_i^0}{-zF} = \frac{RT}{zF} \ln K,$$

where K is the equilibrium constant of the cell reaction, i.e., it contains information about the equilibrium. If one of the half-cells (electrode in the broader sense) in the electrochemical cell is in equilibrium, it can be used for reference purposes. Then the potential of the other half cell is called the electrode potential relative to this reference electrode. *The electrode potential is a potential difference, i.e., the voltage, relative to a reference electrode.*

The standard hydrogen electrode (SHE) was chosen as the general reference electrode, in which the oxidation of molecular hydrogen to solvated protons takes place, and all components are in a standard state at a given temperature. A schematic of such a hydrogen electrode is shown in Figure 1. If the hydrogen ion activity is one and the hydrogen gas pressure is the standard pressure ($p^0 = 1$ bar), then at any temperature (by definition) the potential of SHE is zero. Accordingly, in the Nernst equation for the electrode potential, all terms for the reference electrode are eliminated and thus for the reaction



the cell reaction potential depends only on the half-cell that is investigated,

$$E_{\text{cell}} = \frac{\mu_{\text{red}}^0 - \mu_{\text{ox}}^0}{-zF} - \frac{RT}{zF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}}.$$

Otherwise, electrode potential relative to SHE,

$$E = E^0 - \frac{RT}{zF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}} = E^0 + \frac{RT}{zF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}$$

where E^0 is the standard electrode potential. This is the Nernst equation for the (equilibrium) electrode potential if the reference electrode is the standard hydrogen electrode (SHE).

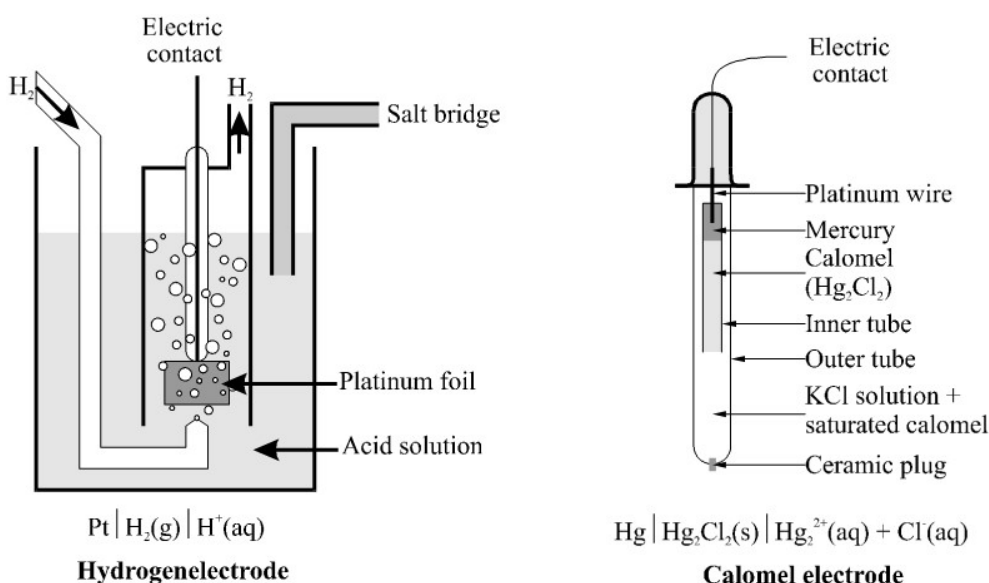


Figure 1: Schematic of a hydrogen electrode and a calomel electrode.

Very often the use of a hydrogen electrode is difficult (imagine a hydrogen gas cylinder and a fume hood for the introduction and removal of hydrogen gas next to the sketch in Fig.1). So we use reference electrodes that are easier to handle. These are most often the so-called second type electrodes, i.e., a metal with a slightly soluble salt of the metal (metal insoluble salt electrode), and an electrolyte whose anion is the same as that of the slightly soluble salt. Examples is the silver – silver chloride electrode, which has a half-cell diagram: Ag(s) | AgCl(s) | AgCl(cc.aq) + KCl(aq), or the calomel electrode: Hg(l) | Hg₂Cl₂(s) | Hg₂Cl₂(cc.aq) + KCl(aq) (Fig.1). In such systems, two (fast equilibrium) processes ensure stable electrode potential,

- charge transfer equilibrium: $\text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}(l)$
- solubility equilibrium: $\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{Cl}^-(aq)$.

As a result, even if a (small) current flows through the cell, the potential of the reference electrode remains constant. The theoretically defined cell reaction potential (or the electrode potential), and the practically measurable cell voltage (potential difference between the cathode and the anode (reference electrode)) can differ from each other for several reasons. If we ensure that no current flows through the cell during the measurement, and the two half-cells are in equilibrium for charge transfer and all other chemical processes, and no other potential difference develops between the half-cells, then the measurable maximum cell voltage (electromotive force, E_{MF}) is equal to the cell reaction potential, thus, to the electrode potential against a given reference electrode. If the reference electrode is not SHE, then the measured electrode potential (E_{meas}) can be calculated against SHE ($E(\text{vs SHE})$), since

$$E_{\text{meas}}(\text{vs Ref}) = E(\text{vs SHE}) - E_{\text{Ref}}(\text{vs SHE}).$$

The electrode potentials of reference electrodes against SHE as a function of temperature and composition can be found in different tables (e.g., for calomel electrode, see Appendix). The Nernst equation for the electrode potential includes the activities of the components,

$$a_i = \gamma_i \frac{c_i}{c^0},$$

where γ_i is the activity coefficient, c_i is the concentration and c^0 is the standard concentration (1 mol/dm³). It is not always possible to determine activity because often only concentrations can be determined by analytical methods, not individual activity coefficients. Thus, in practice, the Nernst equation is used in the form

$$E = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{\text{ox}} \cdot c_{\text{ox}}}{\gamma_{\text{red}} \cdot c_{\text{red}}} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{\text{ox}}}{\gamma_{\text{red}}} + \frac{RT}{zF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}} = E^{0'} + \frac{RT}{zF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}} \quad (1)$$

where $E^{0'}$ is the so-called formal potential. This includes the ratio $\gamma_{\text{ox}}/\gamma_{\text{red}}$ under the given experimental conditions. In electrochemical kinetics, for example, the rate coefficient of the reaction rate of the charge transfer process is related to this formal potential. If we can keep the ratio $\gamma_{\text{ox}}/\gamma_{\text{red}}$ constant in a given series of experiments, then the formal potential is a similar thermodynamic parameter as the standard electrode potential. It is clear that

$$\lim_{c \rightarrow 0} E^{0'} = E^0, \quad \text{since}$$

$$\lim_{c \rightarrow 0} \gamma_{\text{ox}} = \lim_{c \rightarrow 0} \gamma_{\text{red}} = 1.$$

In practice, therefore, the standard electrode potential can be determined by extrapolating the formal potential to zero concentration. Keeping the activity coefficients constant is most likely if the ionic strength of the solution (I) is kept constant. Ionic strength expresses the cumulative effect of ions in the system and it is defined as

$$I = \frac{1}{2} \sum_{i=1}^n c_i \cdot z_i^2$$

where c_i is the concentration of the i -th ion, z_i is its charge number, and n is the number of different ions.

2 Experimental

For the measurements, assemble the electrochemical cell shown in Fig. 2. Use a calomel electrode containing 1 M KCl (so-called normal calomel electrode, NCE) as a reference electrode. The two half-cells should be connected by a KCl salt bridge, which on one hand prevents the mixing of electrolyte solutions and on the other hand ensures that no diffusion potential develops between the two half-cells, i.e., the measured E_{MF} really be the difference in electrode potentials. For the redox electrode tested, use solutions of constant ionic strength in which the ratio of the concentrations of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ differs, and measure the cell potential (electromotive force) at these ratios.

To prepare the stock solutions, the instructor will tell you the ionic strength during the measurement (between 0.05–0.1 M). *Unless the instructor says otherwise*, $I = 0.075$ M. Two stock solutions must then be prepared from the solids salts by weighing (relative atomic masses can also be found in the Appendix):

A: 100 cm³ K₃[Fe(CN)₆] solution of $c_{\text{ox},0}$ concentration

B: 100 cm³ K₄[Fe(CN)₆] solution of $c_{\text{red},0}$ concentration.

Since the ionic strengths of the two stock solutions are the same, the ratio of the concentration of the oxidized and reduced form can be changed by mixing them in any proportion at a constant ionic strength. Using the two stock solutions, prepare different ratios of oxidized and reduced forms (by a method similar to titration) as follows.

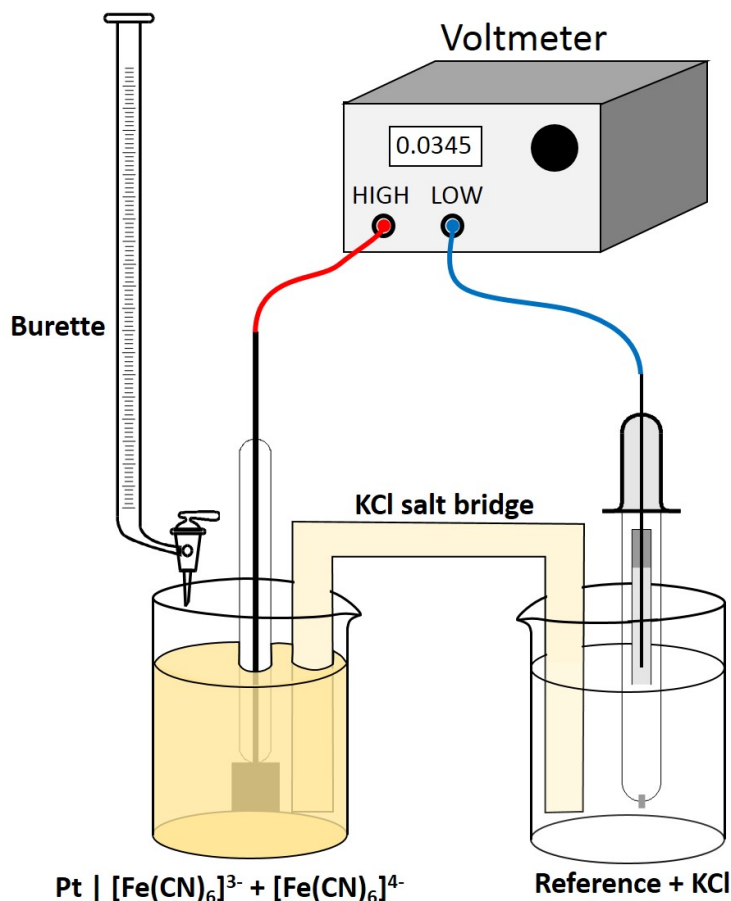


Figure 2: The measuring assembly.

- First, fill one burette with solution A and the other with solution B.
- Measure 25.00 cm^3 solution B with the burette into the beaker belonging to the working electrode of the measuring cell. Then add solution A to solution B and measure E_{MF} between the two electrodes. Calculate the volumes of solution A to be added on the basis of the following considerations.
 1. The figure to be made during the evaluation will show the natural logarithm of the concentration ratios, so the natural logarithms of the volumes must be uniform, i.e., the difference between them must be a constant value.
 2. The minimum and maximum volumes of the solution A should be $1\text{--}24\text{ cm}^3$. Among these, 9 additional titration points must be chosen so that their logarithms are uniformly changing.
 3. The calculation of the volumes should be done before the measurements and it should be checked with the instructor.
- Record the volumes of stock solution A and the measured E_{MF} .

During the measurement, make sure that the entire surface of the platinum part of the working electrode is in the solution. If one end of the salt bridge is yellowed, this end should be in the solution of the redox system and the colorless end should be placed in the KCl solution of the calomel electrode. Also make sure that the working electrode solution is homogeneous at each measuring point. Either stir the solution with a glass rod or move the beaker in a circular motion while holding on the surface of the table until the potential value is constant. During the measurements, it is not a problem if you deviate slightly from the volumes given in the table (previously calculated), but the values of the added volumes read as accurately as possible should be entered in the report and calculated with them in the evaluation. Try to add solution A from the burette so that no broken droplets remain at the tap opening,

thus reducing the experimental error. For each measurement, wait until the voltage is constant before reading.

- After the first series of measurements, replace the beaker of the working electrode, measure 25.00 cm³ of solution A from the first burette into the new beaker, then add solution B from the second burette according to the volumes calculated for the previous titration.
- Repeat the experiments so that the ionic strength of the stock solutions is between 0.1 and 0.2 M. *Unless the instructor says otherwise, I = 0.15 M.*
- Repeat the experiments once more so that the ionic strength of the stock solutions is between 0.2 – 0.3 M. *Unless the supervisor says otherwise, I = 0.30 M.*
- At the end of the measurements, the temperature in the lab has to be read and recorded.

3 Evaluation

- The molar masses, the measured data and the calculations required to apply Eq. 1 are summarized according to Table 1.

Table 1: Summary of the measured data.

$$M_r(K_3[Fe(CN)_6]) = \dots, M_r(K_4[Fe(CN)_6] \cdot 3H_2O) = \dots, [KCl]_{NCE} = \dots M,$$

$$c_{ox,0} = \dots M, c_{red,0} = \dots M, T_{lab} = \dots ^\circ C = \dots K$$

$V_{solA} (cm^3)$	$V_{solB} (cm^3)$	$E_{MF} (V)$	$c_{ox}(M)$	$c_{red}(M)$	$\frac{c_{ox}}{c_{red}}$	$\ln \left(\frac{c_{ox}}{c_{red}} \right)$

- Based on the data in the table, make the $E_{MF} - \ln(c_{ox}/c_{red})$ graphs for each ionic strengths, fit straight lines, and determine the interceptions and slopes together with their standard deviations (see Appendix; Excel LINEST function, Origin, QtiPlot, etc.). Within a series of measurements, the data of the two titrations are plotted together on a graph because they belong to the same curve. The two titrations are only necessary for the measurability of the wider concentration range.
- Calculate the potential of the reference electrode $E_{Ref}(vsSHE)$ from the concentration of the KCl solution and the temperature using the data in the Appendix. *Attention: the calculated value will possess standard deviation.*
- From the slopes of the fitted lines, determine the slope of the Nernst equation and its standard deviation (see Appendix: Standard deviation propagation). Compare the calculated value to the theoretical one.
- From the intercepts and the value of $E_{ref}(vsSHE)$, calculate the formal potential of the investigated redox system with respect to SHE at each ionic strengths. Also give the standard deviation of these potential values (see Appendix: Standard deviation propagation). How does the formal potential change with decreasing ionic strength in the investigated system? Compare the values obtained from your measurements to a standard potential value given in the literature and interpret the differences. The source of the literature data should also be provided.

Questions

1. What is a redox electrode?
2. What is the cell reaction potential and what is the electrode potential?
3. Give the Nernst equation for the electrode potential of a redox electrode.
4. What are the standard electrode potential and the formal potential?
5. Give the calomel electrode half-cell diagram. What equilibria control the electrode potential of the calomel electrode?
6. What is electromotive force?
7. Why do we use a salt bridge during the measurements?
8. Which redox system do you examine during the practice and what data do you determine from your measurements?
9. The electrode potential must be measured at four titration points. The minimum is 0.80 cm^3 , the maximum is 12.00 cm^3 . What volume belongs to the remaining two points if the logarithms of the volumes change uniformly?
10. The concentration of a $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution is 0.15 M . Calculate the concentration of a solution of the same ionic strength from $\text{K}_4[\text{Fe}(\text{CN})_6]$.
11. We titrate 25.0 cm^3 of 0.012 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution with 0.020 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution. What will be the concentration of the oxidized and reduced forms in the mixed solution after the addition of 16.2 cm^3 ?
12. What is the theoretical slope at 25°C of the $E_{\text{MF}} - \ln(c_{\text{Ox}}/c_{\text{Red}})$ line for the redox system studied in the practice? $R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$, $F = 96485\text{ C mol}^{-1}$.